Ionization of@ (Buckminsterfullerene) by Electron Impact

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Utilising a crossed electron beam-molecular beam collision geometry, mass spectra of C_{60} and C_{70} ions have been obtained for an electron impact energy range of 20 eV to 600 eV. These spectra are dominated by singly and doubly ionized species. The intensity of fragment ions is very weak which is in agreement with previous observations. Ionization efficiency curves for the formation of C_{60}^{+} and C_{60}^{++} have also been obtained near their threshold regions. From these curves appearance energies (A. E.) of these ions have been derived. The A. E. for C_{60}^{+} is found to be 7.8 ± 0.3 eV which agrees well with previous measurements. However, our value of 16.4 ± 0.3 eV for the formation of C_{60}^{++} is much lower than 19.0 ± 0.03 eV obtained by photo-ionization techniques.

Ever since the discovery] of a method for producing large quantities of C_{60} (Buckminsterfullerene) and its availability to the scientific community has become possible, a large number of studies have been directed towards understanding its physical and chemical properties[2-5]. Among them, electron impact ionization of vapor phase C_{60} is of special interest for characterizing the spectroscopic behavior of fullerenes. However, a detailed study of the ionization properties has never been carried out. Luffer and Schram[6] obtained ionization mass spectra of C_{60} and C_{70} at 70 eV electron impact energy. For this purpose they employed a commercial double-focusing mass spectrometer in which the sample was introduced and heated to a temperature of 300 C. In their spectra, they observed singly charged ions of C_{60} and C_{70} which appeared at m/q of 720 and 840, respectively, and doubly charged ions at m/q 360 and 420, respectively. In addition, they found that only C_{60} produced triply charged ions at m/q 240 and it underwent fragmentation by losing successive multiples of C_2 through C_{16}. On the other hand, C_{70} fragmented by losing C_2 and C_4. Luffer and Schram concluded that 95% of the C_{60} ionized with very little fragmentation indicating a very highly stabilized structure with considerable aromatic character. Subsequent mass spectrometric techniques[7-9] derived similar conclusions. These studies were qualitative in nature and were very helpful in understanding the fragmentation properties of fullerenes. The first quantitative measurements were performed by Sai Baba et al [10]11' who determined the absolute values of ionization cross sections at 38 eV electron impact energy. They also measured the appearance energies (A. E.) for the formation of C_{60}^{+} and C_{70}^{+}. The appearance energies for C_{60}^{+} and C_{60}^{++} have also been measured by a variety of other techniques. They are summarized in Table 1. This table shows that there is fairly good agreement between the various results for the A. E. of C_{60}^{+}. However, the measured values of A. E. for the formation of C_{60}^{++} differ considerably.

Since a detailed study of ionization properties of C_{60} and C_{70} for a range of electron impact energies has never been carried out and since there are considerable differences between the various measured values of the appearance energy of C_{60}^{++} we undertook a systematic study of these species. In the following we will present ionization spectra and the appearance energies for single and double ionization of C_{60}.

EXPERIMENTAL

A schematic diagram of the apparatus used in this study is shown Fig. 1. A mixture of (75% C_{60} and 25% C_{70} plus higher fullerenes) powder was filled inside a stainless steel crucible. This mixture was heated by a coaxial heater wire. With this heating arrangement a temperature of about 800 C could be achieved. The crucible had a pin hole at the top from where the vapor of the mixture effused in the form of a beam. Most spectra were obtained when the crucible was heated to a temperature of 400 C. This molecular beam was crossed at 90^{o} by an energy selected beam of electrons . The electron beam was produced by a magnetically collimated electron gun 12 which had an energy spread of less than 0.5 eV. The energy of the electron beam could be varied from about 3 eV to 600 eV in several steps in such a way that the electron beam current remained approximately constant during each step as a function of energy. The electron beam was pulsed at a frequency of 5 kHz and the pulse width was 0.5 μs. As a result of collisions of electrons with the molecular beam, ions were produced. These ions were extracted by an electric field of about 70 v/cm which was obtained by applying a negative voltage between the ion extraction lens and the ion repeller plate. This voltage was reduced to ground potential by applying a positive pulse of about 1 μs duration. Thus, during the passage of the electron beam through the beam interaction region, the total environment around this region was at ground potential. The ion extraction lens was part of a time of flight mass spectrometer (TOFMS) which was used for mass analysis. After passing through the TOFMS, the ions were detected by a spiraltron which converted each detected ion into an electrical pulse. These pulses were amplified and fed to the stop signal of a time to pulse height converter (TPC). The start pulse to this unit was provided by the electron beam pulse. Thus, the TPC measured the flight time of each ion. This information was stored in a pulse height analyzer which identified the mass and any delay in flight time of the ion. A detailed description of the pulsing scheme for the TOFMS system can be found in a publication by Krishnakumar and Srivastava[13].

RESULTS AND DISCUSSION

The mass spectra of C_{60} and C_{70} ions were recorded at electron impact energies of 20, 30,40,50, 60,70, 80, 100, 200,400 and 600 eV. Two representative ones for 70 eV and 200 eV are shown in Fig. 2. It can be seen that singly , doubly and triply charged ions of both species are present. These data were acquired on several different occasions and under different experimental conditions. Earlier mass spectrometric studies had shown[6] that C_{60} and C_{70} predominantly ionized into singly and doubly charged ions with very little fragmentation. Our measurements, which were carried out over a wide range of energies, support their findings. At first, lack of fragmentation may seem unusual because for most small molecules dissociation into fragment ions dominates due to Coulomb repulsion. However, as has been pointed out by Yoo et al. [14], large hydro-carbons[15,16] can maintain larger charge separation without undergoing Coulomb explosion. This property clearly indicates the aromatic nature of fullerenes. The ionization spectrum at higher electron impact energies (100 eV and above) show that the process of dissociative ionization is more efficient for doubly and triply ionized species than for C_{60}^{+}.

Ionization efficiency curves for the production of singly and doubly ionized C_{60} were obtained by varying the energy of the electron beam from 3 eV to 70 eV and by recording the intensities of the two ions as a function of electron beam energy. Magnified portions of these curves near the thresholds of their formation are shown in Figs. 3 and 4.

During the course of our work it was observed that upon heating the crucible water also effused which was initially mixed with the C_{60}/C_{70} powder. Its ion intensity signal was appreciable and continued to be present during the entire experiment which lasted several weeks. However, the water ion intensity decreased steadily. Every time the crucible was filled with a fresh sample of C_{60}/C_{70} the water ion signal was present. We took advantage of this situation to obtain the ionization efficiency curve for water. Since the ionization energy [17,18] of water is accurately known, we used its ionization efficiency curve to calibrate the energy of the electron beam.

The procedure for calibrating the electron beam energy was as follows. The electron beam energy, as measured by a volt meter, was recorded for the position where the ionization efficiency curve began to rise above the constant background. This value was then compared with the accurately known value (12.612 ± 0.010)[17] of the ionization energy of water and a value of correction factor was obtained. The above procedure was repeated for the formation of C_{60}^{+} and C_{60}^{++}. For both curves, (Figs. 3 and 4), this correction was applied. The true values of A. E. for C_{60}^{+} and C_{60}^{++} were thus obtained. Although the spread in the electron beam energy was estimated to be about 0.5 eV, it was estimated that the values obtained by applying the above procedure were accurate to within 0.3 eV. Present values for A. E.'s along with previously measured ones are presented in Table 1 where the various methods employed for the measurements are also indicated.

As mentioned earlier, the values of appearance energies for C_{60}^{+}, obtained by various experimental methods agree well with each other within the experimental *error* limits of each method. However, the values for the formation of C_{60}^{++} widely disagree. The photo-ionization method, which has been applied in the past for the determination of A. Es of a variety of species[19] is well established and provides accurate values with high energy resolution. On the other hand, the electron impact method suffers from poor energy resolution. However, the present result (16.4N.3, eV) for the formation of C_{60}^{++} from C_{60} is significantly less (about 2.6 eV) than the value (19.OMI.03, eV) obtained by the photo-ionization method and can not be reconciled. The present value was derived from several sets of data obtained at different experimental conditions. The data for C_{60}^{+}, C_{60}^{++}, and H_2O^{+} were recorded under the same experimental conditions each time. Accuracy of our procedure for obtaining A. E.'s is evidenced by the fact that our value for C_{60}^{+} agrees well with most previous measurements.

There is also a substantial disagreement between the various values of A. E.'s for the formation of C_{60}^{++} from C_{60}^{+} (Table 1). If the most recent value of A. E., 7.57 ± 0.01, obtained by the photo-ionization method[21] is added to the recent value[29] of 11.9 eV for the formation of C_{60}^{++} from C_{60}^{+}, then the value of A. E. for the ionization of C_{60} into C_{60}^{++} is equal to 19.47 eV which is in good agreement with the value of 19.0 ± 0.03 eV measured by the photo-ionization method[20]. Similarly, if the present value of A. E. (7.8 ± 0.3) for the formation of C_{60}^{+} from C_{60} is added to the most recent value of 8.5 ± 0.5 eV for the formation of C_{60}^{++} from C_{60}^{+} obtained by charge stripping method[30] then the result is 16.3 eV which is in excellent agreement with the present value of 16.4 eV.

The ionization efficiency curve for C_{60}^{++} (Fig. 4) clearly shows two slopes, By visually drawing a mean straight line through the first part of this curve we find the appearance energy to be 16.4 eV. However, if such a mean straight line for the second part of the curve is extended to cross the x-axis then it indicates an A. E. of about 19.5 eV which is in agreement with the photo-ionization value. Perhaps the differences in the values of A. E.'s obtained by electron impact and photo-ionization lie in the mechanism through which the ionization takes place. Although there are several theoretical calculations 22-27 on the ionization energies of C_{60} and C_{60}^{+}, none of them specifically throw light on the direct mechanism of formation of C_{60}^{++} from C_{60}. Rosen and Wastberg[24] calculated, using the local density approximation, the first ionization energies to be 6.9 and 7.8 eV by using two different approaches. For the ionization of C_{60}^{+} into C_{60}^{++} they obtained values of 10.1 and 10.8 eV, respectively, by using the same two approaches. Thus, according to them the lowest energy for the formation of C_{60}^{++} from C_{60} is 17 eV. Chang et al.[26] performed ab initio restricted Hartree-Fock calculations to compute ionization energies by taking differences between the C_{60} ground state and all corresponding ion (C_{60}^{+}) states (ΔSCF) and by Koopmans' theorem. The first ionization energy, as obtained by them, was 8.14 eV and for the C_{60}^{++} it was 11.24 eV, both in the ΔSCF method. Most recent calculations of Gallop [27] find the first ionization energy to be 7.6 eV and the ionization energy for C_{60}^{+} to be 11.2 eV.

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FIGURE CAPTIONS

Fig. 1. A schematic diagram of the experimental apparatus.

Fig. 2. Time of flight spectra of C_{60} ions at 70 eV and 200 eV.

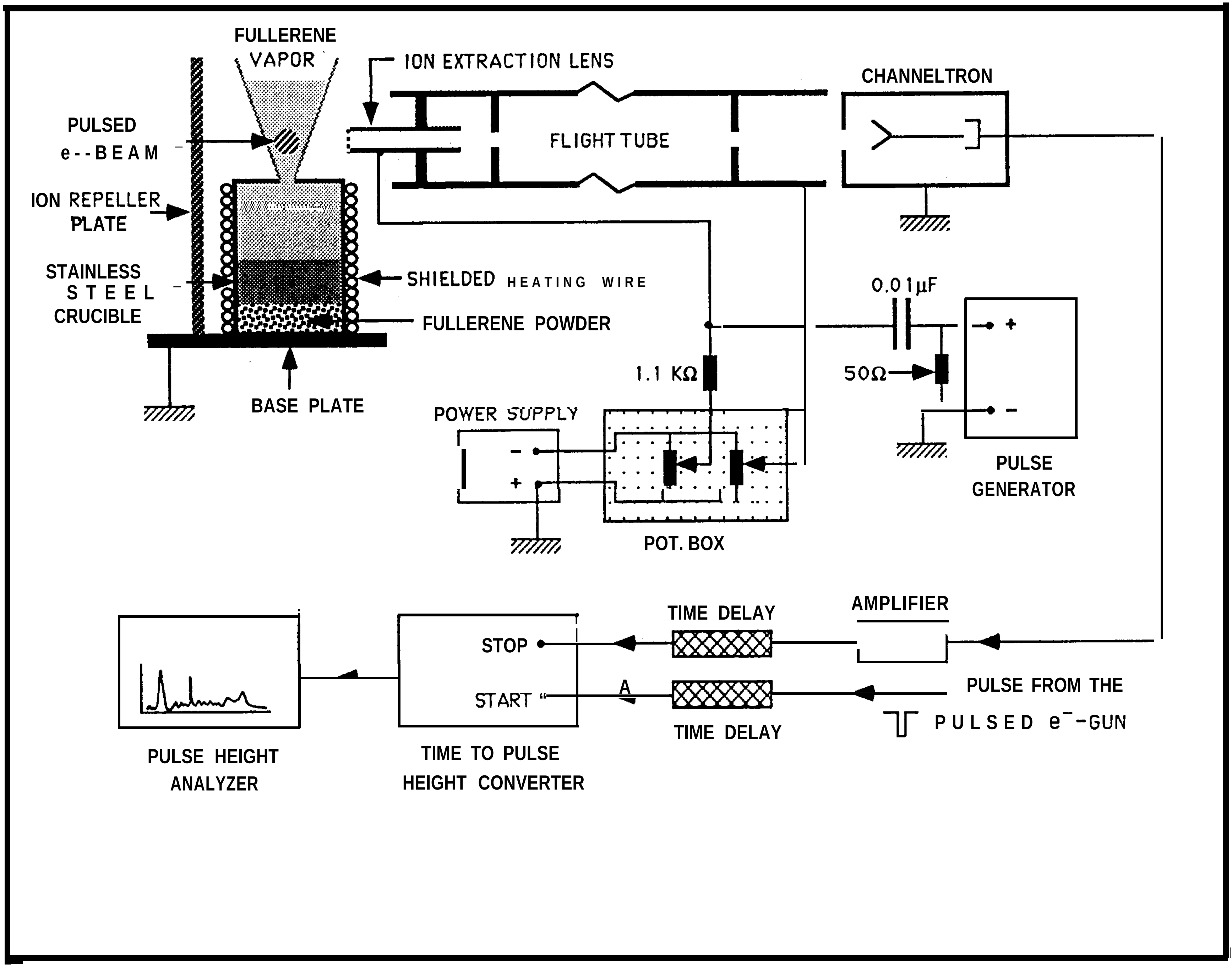
Fig. 3. Ionization efficiency curve for the formation of C_{60}^{+} from C_{60} near the threshold region.

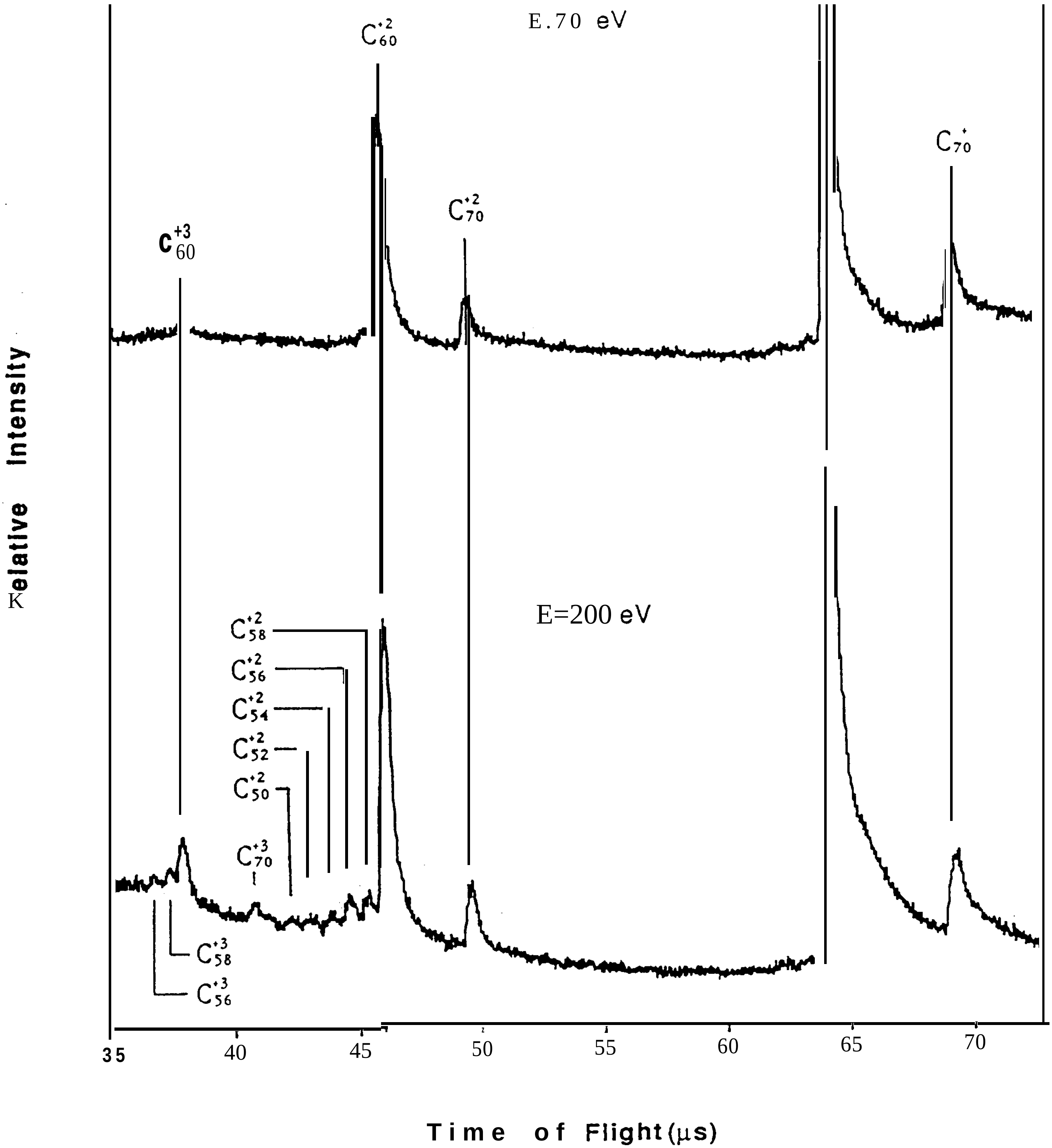
Fig. 4. Ionization efficiency curve for the formation of C_{60}^{++} from C_{60} near the threshold region.

TABLE 1

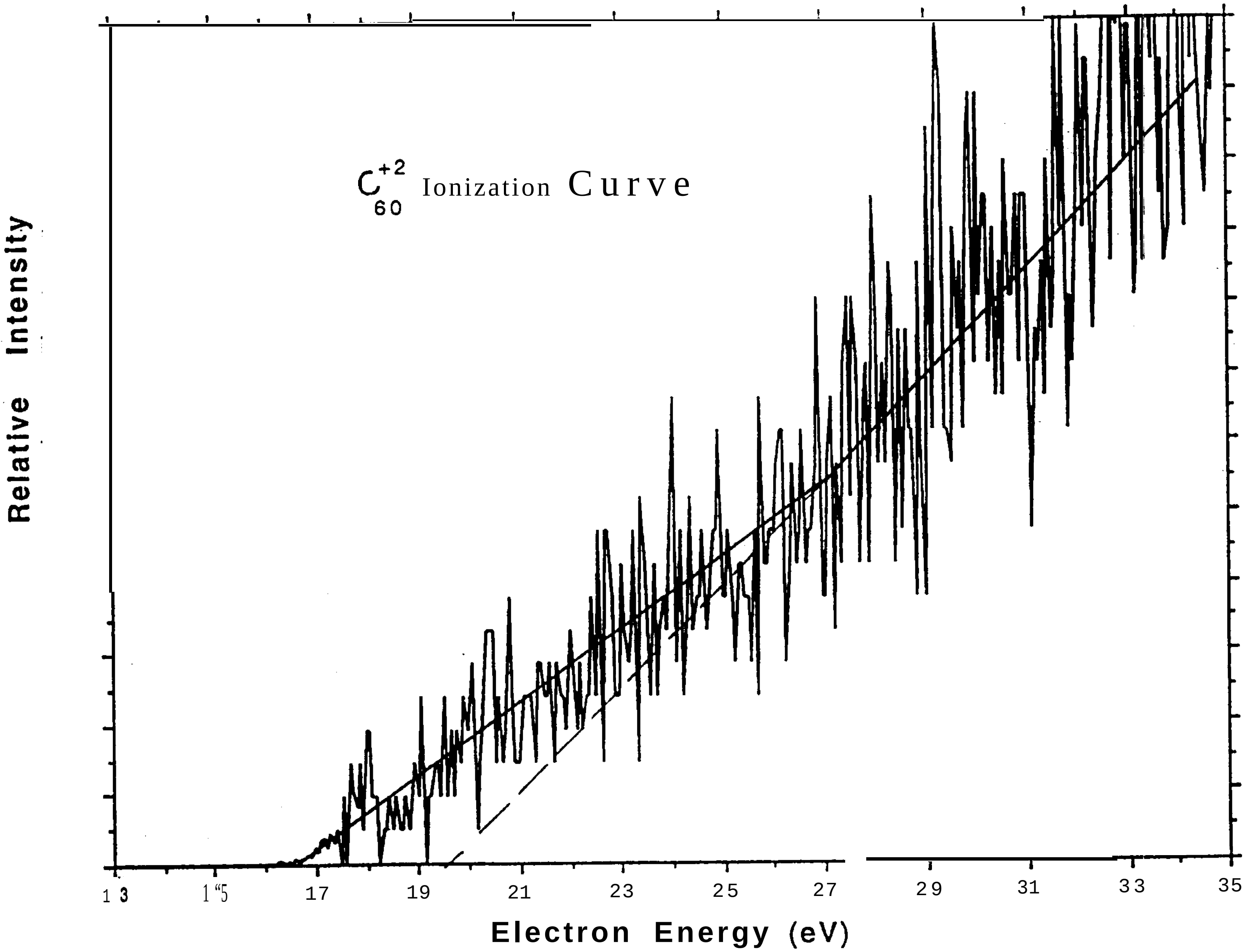
Experimentally determined appearance energies (A. E.) of C_{60}^{+} and C_{60}^{++} in eV.

Ref.	C_{60}^{+}/C_{60}	C_{60}^{++}/C_{60}	C_{60}^{++}/C_{60}^{+}	Mehtod
31	7.6 1±0.11	--	--	Charge transfer bracketing technique (1991)
32	7.61 ±0.02			Photo-electron, gas phase target(1991)
33	--	--	9.7±0.2	Charge transfer bracketing technique(1991)
8	--		12.25	Deduced from translational energy loss in a charge stripping reaction(1991)
21	7.54±0.04	--	--	Photo-ionization(1992)
10	8.504050	--	--	Electron impact(1992)
14	7.57±0.01	--	--	Photo-ionization(1992)
29	--	--	11.9	Charge stripping(1992)
30	--	--	8.5±0.5	Charge Stripping(1992)
20	--	19.0±0.03	--	Photo-ionization(1993)
Present	7.840.3	16.4±0.3	--	Electron impact


FULLERENE VAPOR
ION EXTRACTION LENS
CHANNELTRON
PULSED e--BEAM
FLIGHT TUBE
ION REPELLER PLATE
STAINLESS STEEL CRUCIBLE
SHIELDED HEATING WIRE
FULLERENE POWDER
0.01μF
BASE PLATE
1.1 KΩ
50Ω
POWER SUPPLY
PULSE GENERATOR
POT. BOX
AMPLIFIER
TIME DELAY
STOP
START
A
PULSE FROM THE PULSED e⁻-GUN
TIME DELAY
PULSE HEIGHT ANALYZER
TIME TO PULSE HEIGHT CONVERTER



E.70 eV
E=200 eV
C_{60}^{+3}
C_{60}^{+2}
C_{70}^{+2}
C_{70}^{+}
C_{58}^{+2}
C_{56}^{+2}
C_{54}^{+2}
C_{52}^{+2}
C_{50}^{+2}
C_{70}^{+3}
C_{58}^{+3}
C_{56}^{+3}
Relative Intensity
35
40
45
50
55
60
65
70
Time of Flight (μs)



C_{60}^{+2} Ionization Curve
Relative Intensity
13
15
17
19
21
23
25
27
29
31
33
35
Electron Energy (eV)